

Review paper

Understanding Static and Dynamic Heterogeneities in Confined Water

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Dedicated to Prof. Dr. Alfons Geiger on the occasion of his 65th birthday

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Confined Water / Widom Line

We report recent efforts to understand the new MIT-Messina experimental discovery of a dynamic crossover at low temperatures in confined water. Preliminary calculations are not inconsistent with one tentative interpretation of this dynamic crossover as resulting from the system passing from the high-temperature high-pressure "HDL" side of the Widom line (where the liquid might display fragile behavior) to the low-temperature low-pressure "LDL" side of the Widom line (where the liquid might display strong behavior). The Widom line - defined to be the line in the pressure-temperature plane where the correlation length has its maximum - arises only if there is a critical point. Hence interpreting the MIT experiments in terms of a Widom line is of potential relevance to testing experimentally, for *confined* water, the liquid-liquid critical point hypothesis.

1. Introduction

This author's water research began 30 years ago - when, under the auspices of a Guggenheim Fellowship, he learned "the facts of water" under the tutelage of three mentors, J. Teixeira, A. Geiger, and C. A. Angell. The most puzzling facts dealt with understanding what are the various experimentally-observed crossovers and non-monotonic behavior telling us about the underlying physics and chemistry of water. How can we understand the observed facts that as one cools below 46°C and 35°C, respectively, the volume and entropy fluctuations (com-

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pressibility and specific heat) increase? Even more puzzling is the Angell discovery that these increase can be fit by power laws with the identical singularity temperatures, about $228\text{K} \pm 5\text{K}$ [1–20]. This temperature is within the experimentally-inaccessible "No-Man's land," where bulk water is normally found only in its crystalline phase. Nonetheless, the water research community has remained fascinated with these apparent divergences for more than 30 years [13]. Despite this widespread interest, and despite the huge influence of this "unattainable" apparent singularity (appearing in the *metastable* region of bulk water) on functions in the *stable* region, an accepted cause for the observed behavior has not been found.

In order to understand what the Angell phenomena might be telling us, Teixeira and the author developed a fairly crude qualitative picture [21,22] which ultimately has been improved considerably (called the "singularity-free" hypothesis [23,24]). It envisages only *apparent* singularities, due to anticorrelated volume and entropy fluctuations which arise from correlations in locally-structured "spatial heterogeneities." This qualitative picture was confirmed by Geiger who analyzed extensive simulations of the ST2 model [25–34]. In 1992, it was conjectured, on the basis of simulations using the ST2 and TIP4P potentials by the authors's students and postdocs, that these spatial heterogeneities might actually "condense," forming thereby a low-density liquid phase below a line of liquid-liquid (LL) phase transition [35–38], and that the line of apparent singularity temperature discovered by Angell and co-workers coincides with the analytic continuation (the "Widom line") of the line of LL phase transitions extending above the hypothesized LL critical point [39–41].

The LL phase transition hypothesis has the feature that, if it were valid, it would connect the anomalies of water, such as the presence of not one but rather two forms of glassy water. Hence others [42–61] have begun to test the possible validity of this still rather tentative conjecture, and we have ourselves participated in some of these tests [62–94].

To understand "why" water might display such a novel feature, which Stuart Rice calls "liquid polymorphism" [18], we have attempted to create various tractable models that display a LL phase transition, and to find solutions of these models using both analytic solution of the simplest cases and approximate solution (such as by integral equation approaches) for the more complex cases. Results thus far are not definitive, and one goal of our current research is to attempt to seek new avenues whereby definitive work can be undertaken to test the truth or falsehood of the LL phase transition hypothesis. In collaboration with many others, we are focusing largely on understanding new experiments on *confined* water, where the LL critical point - if it exists - is in the stable region of the phase diagram. Confined water differs from bulk water, but nonetheless is a material of interest in its own right. Moreover, the collective features may be quite related, as in phase transition models where the collective features of diverse systems are related by the concept of universality [14,95].

Liquid Polymorphism (sometimes called by the neologism *polyamorphism* or simply *amorphous polymorphism*) refers to the existence of distinctly different amorphous forms of a pure substance, and is a topic of huge current interest in chemistry and materials science. Water's hypothesized LL phase transition, an example of polymorphism, is difficult to detect *experimentally* because water freezes readily to crystalline ice below the homogeneous nucleation temperature T_H , and T_H is above the temperature T_C of the hypothesized critical point. Because it is so difficult to make experiments in the *No-Man's land* below T_H , any kind of information in this region has the potential of being extremely valuable. Previous work largely concerns *bulk* water, but much current work largely concerns *confined* water, since for appropriate forms of confinement, the No-Man's land is very small or may not even exist [17].

2. Indirect experimental probe of the region between T_H and T_X ("No-Man's land")

Mishima used a new method to probe the region below T_H and so provided a test for the hypothesized LL transition [47]. This paper - and its sequel [48] - provide an indirect experimental probe of a large region of the P-T phase diagram that previously could not be explored, the region below T_H and above the crystallization temperature T_X (about 150 K). This "No-Man's Land" is of considerable general interest because the hypothesized LL critical point, if it exists at all, is believed to lie in this region. Reference [47] found that along the decompression-induced melting (DIM) line of ice IV, a discontinuity in the slope occurs, a significant finding since a melting line must have a smooth behavior unless it intersects some other relevant line in the phase diagram such as a line of LL phase transitions. Mishima measured metastable DIM curves of other high-pressure forms of ice and constructed the Gibbs potential surface of the liquid by knowing the Gibbs potential of the melting lines of each of the high-pressure ices and then interpolating between this set of lines. He found that a "crease" emerges on the Gibbs potential surface of the liquid. Accordingly, a large volume change appears on the equation of state $V(P,T)$ of liquid, given by the pressure derivative $\partial G/\partial P$. Moreover, the location of the kink in the DIM line of ice IV is exactly the same as the location of the LL transition on the Gibbs surface.

The LL phase transition hypothesis is of interest outside the domain of confined water because the underlying mechanism responsible for the LL phase transition suggests that for other liquids with local tetrahedral symmetry, analogous *anticorrelated* entropy/volume heterogeneities could appear and might indeed, under appropriate conditions, condense out as a low-density liquid phase [58,96]. This possibility has motivated high-quality work on other materials [97–108] such as Si, SiO₂, C, and, P. For P [98,108], the line of LL phase transitions has been probed experimentally. Recent experiments detect a first-order LL phase transition in yttrium oxide-aluminum oxide melts [109]. Thus it is quite

possible that the LL phase transition hypothesis fails for water, but nonetheless could prove useful in guiding research on other materials [12,102].

3. Direct experimental probe of the "No-Man's land" region for confined water

Recently, the MIT group of Professor S.-H. Chen succeeded in probing the No-Man's land by using the trick of confining liquid water to nanopores of diameter 16–20Å [49,50,110–119]. The Boston University group, in collaboration with Professor Chen, offered a possible interpretation of their experimental results [40]. Specifically, they found a correlation between the dynamic fragility transition and the locus of specific heat maxima C_p^{\max} and thermal expansion coefficient maxima α_p^{\max} [73,78,120,121] ("Widom line") emanating from the critical point. Their preliminary findings are consistent with a possible relation between the hypothesized LL phase transition and the transition in the dynamics recently observed in neutron scattering experiments on confined water. More generally, they are finding that this connection between C_p^{\max} and the dynamic crossover may not be limited to the case of water, a hydrogen bond network forming liquid, but could be a more general feature of crossing the Widom line, and can also apply to confined water.

4. NMR proton chemical shift measurements as a new method for estimating the configurational part of the heat capacity $C_p(T)$

Recently, Mallamace and collaborators performed NMR proton chemical shift measurements as a new method for estimating the configurational part of the heat capacity $C_p(T)$ [122–124]. This study introduces NMR proton chemical shift measurements as a new method for estimating the configurational part of the heat capacity $C_p(T)$ that results from the hydrogen bonding of the water molecules. To test this new method, they measured the water proton chemical shift as a function of temperature by using the same confining system of recent nanoconfinement experiments [40,49,50,125,126,127]. Specifically, they measured using NMR the proton chemical shift δ of supercooled nanoconfined water in the temperature range $195 < T < 350$ K. Since δ is directly connected to the magnetic shielding tensor, they discussed the data in terms of the local hydrogen-bond geometry and order. They argue that the derivative $-(\partial \ln \delta / \partial T)_P$ should behave roughly as the constant pressure specific heat $C_p(T)$, and they confirm this argument by detailed comparisons with literature values of $C_p(T)$ in the range 290K–370K. They found that $-(\partial \ln \delta / \partial T)_P$ displays a pronounced maximum upon crossing the locus of maximum correlation length at about 240 K, consistent with the liquid-

liquid critical point hypothesis for water, which predicts that $C_p(T)$ displays a *maximum on crossing the Widom line*. Because the NMR technique also gives the chemical shift of each sample nucleus with non-zero spin, such an approach may be applicable to more complex materials.

5. Possible relevance of skin of water surrounding a macromolecule to its low-temperature glass transition

Both experiments and computer simulation studies have shown that hydrated proteins undergo a "glass-like" transition near 200 K [128–132], above which proteins exhibit diffusive motion, and below which the proteins are trapped in harmonic modes. An important issue is to determine the effects of hydration water on this dynamical transition [133–136]. Experiments and computer simulations suggested that when a protein is solvated, the protein glass transition is strongly coupled to the solvent, leading to the question of whether the protein glass transition is directly related to a dynamic transition in the surrounding solvent [137].

Using molecular dynamics simulations, Kumar and collaborators [113–115,138] investigated the relation between the dynamic transitions of biomolecules (lysozyme and DNA) and the dynamic and thermodynamic properties of hydration water. They found that the dynamic transition of the macromolecules, sometimes called a "protein glass transition", occurs at the temperature of dynamic crossover in the diffusivity of hydration water, and also coincides with the maxima of the isobaric specific heat C_p and the temperature derivative of the orientational order parameter. We related these findings to the hypothesis of a liquid-liquid critical point in water: our simulations are consistent with the possibility that the protein glass transition results from crossing the Widom line, which is defined as the locus of correlation length maxima emanating from the hypothesized second critical point of water.

6. Translational and rotational dynamic heterogeneities

At temperatures where liquids have a diffusion constant similar to that of ambient temperature water, the translational and rotational diffusion, D_t and D_r , respectively, are well described by the Stokes-Einstein (SE) relation $D_t = k_B T / 6\pi\eta R$ and the Stokes-Einstein-Debye (SED) relation $D_r = k_B T / 8\pi\eta R^3$. Here T is the temperature, η the viscosity, k_B the Boltzmann constant and R is the "molecular" radius. Recently, the limits of the SE and SED relations have been an active field of experimental [125,139–141], theoretical [142–146] and computational [127,147–,157] research. The general consensus is that the SE and SED relations hold for low-molecular-weight liquids for $T \geq 1.5 T_g$, where T_g is the glass transition temperature. For $T \leq 1.5 T_g$, deviations from either one or both of the

SE and SED relations are observed. Experimentally, it is found that the SE relation holds for many liquids in their stable and weakly supercooled regimes, but when the liquid is deeply supercooled it overestimates D_t relative to η by as much as two or three orders of magnitude, a phenomenon usually referred to as the "breakdown" of the SE relation. The situation for the SED relation is more complex. Some experimental studies found agreement with the predicted values of the SED relation even for deeply supercooled liquids [16,158], while others claim also a breakdown of the SED relation to the same extent as for the SE relation [139,159,160]. The failure of these relations provides a clear indication of a fundamental change in the dynamics and relaxation of the system. Indeed, the changing dynamics of the liquid as it approaches the glass transition is well documented, but not yet fully understood [15,161].

There is a growing body of evidence [162–165] that, upon cooling, a liquid does not become a glass in a spatially homogeneous fashion. Instead the system is characterized by the appearance of dynamical heterogeneities [16,158,162–170]. In the "dynamical heterogeneities" (DH) view, the motion of atoms or molecules is highly spatially correlated. This phenomenon is often called "spatially heterogeneous dynamics", since there are spatial regions in which the structural relaxation time can differ by orders of magnitude from the average over the entire system. The presence of these DH has been argued to give rise to the breakdown of the SE relation [142,146]. Since the derivation of the Einstein relation assumes uncorrelated motion of particles, it is reasonable that the emergence of correlations could result in a failure of the SE relation. The aim of the present work is to assess the validity of the SE and SED relations in the SPC/E model of water, and consider to what extent the DH contribute to the SE and SED breakdown.

Computer simulations have been particularly useful for studying DH (e.g., see Refs. [171–176]) since simulations have direct access to the details of the molecular motion. For water, the existence of regions of enhanced or reduced mobility has also been identified [176]. In particular, Ref. [176] identifies the clusters of molecules with greater *translational* (or center of mass) mobility with the hypothesized "cooperatively rearranging regions" of the Adam-Gibbs approach [177,178]. For water, those DH are also accompanied by spatial heterogeneities [25,179]

Mazza and collaborators [119,180–185] found that both the SE and SED relations break down at low temperature. To explore the relationship between these breakdowns and dynamical heterogeneities (DH), they also calculate the SE and SED relations for subsets of the 7% "fastest" and 7% "slowest" molecules. They found that the SE and SED relations break down in both subsets, and that the breakdowns occur on all scales of mobility. Thus these breakdowns appear to be generalized phenomena, in contrast with a view where only the most mobile molecules are the origin of the breakdown of the SE and SED relations, embedded in an inactive background where these relations hold. At low temperature, the SE and SED relations in both subsets of molecules are

replaced with "fractional" SE and SED relations, $D_t \sim (\tau/T)^{-\xi_t}$ and $D_r \sim (\tau/T)^{-\xi_r}$, where $\xi_t \approx 0.84$ (< 1) and $\xi_r \approx 0.75$ (< 1). They also found that there is a decoupling between rotational and translational motion, and that this decoupling occurs in both fastest and slowest subsets of molecules. Further, they found that when the decoupling increases upon cooling, the probability of a molecule being classified as both translationally and rotationally fastest also increases. To study the effect of time scale for SE and SED breakdown and decoupling, they introduce a time-dependent version of the SE and SED relations, and a time-dependent function that measures the extent of decoupling. Their results suggest that both the decoupling and SE and SED breakdowns originate at the time scale corresponding to the end of the cage regime, when diffusion starts. This is also the time scale when the DH are more relevant.

7. Possible cause of the experimentally-observed breakdown of the Stokes-Einstein relation

In the Cozzarelli-Prize winning paper, the MIT group's experiments very recently showed that supercooled water exhibits a breakdown of the Stokes-Einstein relation between the diffusion constant D and the alpha relaxation time τ_α [125]. For simulated water, we found that the temperature of the decoupling of diffusion and alpha relaxation correlates with the temperature of the maximum in specific heat that occurs at the Widom line $T_W(P)$. Specifically, they found that their results for $D\tau_\alpha/T$ collapse onto a single master curve if temperature is replaced by $T - T_W(P)$, where $T_W(P)$ is the temperature where the constant-pressure specific heat achieves a maximum. Moreover they found that the size of the mobile molecule clusters (dynamical heterogeneities) increases sharply near $T_W(P)$. The crossover from the less structured locally high density liquid (HDL) environment at high T to the more structured locally low density liquid (LDL) environment as $T \rightarrow T_W(P)$ appears to be correlated with both the breakdown of the Stokes-Einstein relation and the growth of dynamic heterogeneities.

The breakdown of the SE relation is usually understood by the fact that diffusion at low temperatures is dominated by regions of fast moving molecules while the relaxation of the system as a whole is dominated by slow moving molecules. Consistent with this, Kumar et al. [125,127,156] found that the growth of mobile particle clusters occurs near the Widom line and the breakdown of the SE ratio for $P < P_C$. Thus the SE breakdown in water is consistent with the LL-critical point hypothesis [1,2,11,47,186]. Their results are also consistent with recent experimental findings in confined water [49,50,125,156]. The onset of the fractional Stokes-Einstein effect has recently been studied [187].

8. Experimental method of testing the singularity-free scenario

Using Monte Carlo simulations and mean field calculations for a cell model of water, Franzese et al. [65–67,119,188–190] found that both the LL critical point and singularity free (SF) scenarios exhibit a dynamic crossover at a temperature close to $T(C_P^{\max})$, which decreases for increasing P . They interpret the dynamic crossover as a consequence of a local breaking and reorientation of the bonds for the formation of new and more tetrahedrally oriented bonds. Above $T(C_P^{\max})$, when T decreases, the number of hydrogen bonds increases, giving rise to an increasing activation energy E_A and to a non-Arrhenius dynamics. As T decreases, entropy must decrease. A major contributor to entropy is the orientational disorder, that is a function of p_B , as described by the mean field expression for ΔS . They found that, as T decreases, p_B - hence the orientational order - increases. They found that the rate of increase has a maximum at $T(C_P^{\max})$, and as T continues to decrease this rate drops rapidly to zero - meaning that for $T < T(C_P^{\max})$, the local orientational order rapidly becomes temperature-independent and the activation energy E_A also becomes approximately temperature-independent. Corresponding to this fact the dynamics becomes approximately Arrhenius.

They found that the crossover is approximately independent of the pressure consistent with our calculations of an almost constant number of bonds at $T(C_P^{\max})$. In both scenarios, E_A and T_A decrease upon increasing P , but the P dependence of the quantity $E_A/(k_B T_A)$ has a dramatically different behavior in the two scenarios. For the LL critical point scenario it increases as $P \rightarrow P_C$, while it is approximately constant in the SF scenario. We interpret this difference as a consequence of the larger increase of the rate of change of p_B in the LL critical point scenario, where p_B diverges at finite T_C , compared to the SF scenario, where p_B can possibly diverge only at $T = 0$. Since experiments can detect local changes of water structure from HDL-like to LDL-like, (e.g., [191]), it is possible that our prediction on the dynamic consequences of this local change may be experimentally testable.

9. Ongoing work

When data begin to deviate from extrapolations there must be an underlying reason for the deviation. These deviations include phenomena at temperatures as high as 46°C and 35°C (sudden change of slope of isothermal compressibility and isobaric specific heat, respectively) and maxima in thermodynamic functions such as the coefficient of thermal expansion (at about 225K) [73,78,120,121,192]. Thus far there is no coherent and accepted explanation for these anomalies - even the anomalies that occur at biologically-relevant temperatures. It is unfortunate that chemistry textbooks cannot offer students a coherent explanation of water's behavior, even though water is "essential for life", and

even though very small perturbations on pure water are incompatible with life (such as substituting water by heavy water).

One question we will focus on is "what features of bulk water survive confinement"? Certainly the hydrogen bond network is perturbed, which explains why MCM-41 nanoconfined water remains liquid down approximately 100 degrees lower than bulk water. But what about the collective properties of water [193–199] which rely on the direct cooperative interactions among water molecules? How are these perturbed by confinement? For example, a confined magnet or fluid near its critical point behaves exactly as a bulk magnet or fluid until the system is so close to the critical point that its correlation length (the length scale over which the spins or molecules are correlated) increases to reach the size of the confining system. The MIT/Messina water experiments on MCM-41 confinement are typically carried out on tubes of diameter about 1.5–2.0 nm. Hence if we apply the principles of phase transition theory, the cooperative properties of the system should resemble those of a bulk system for temperatures extremely close to the critical point, about 1 percent away.

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